

**Study of Chloride in the Passive Film on Aluminum Prior to Pitting Corrosion**

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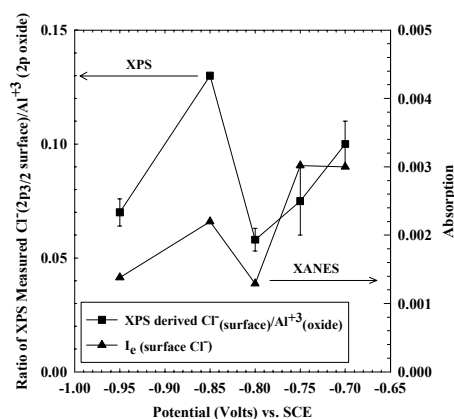
Beamline(s): X19A

**Introduction:** Aluminum (Al) experiences pitting corrosion at a critical pitting potential in 0.1 M NaCl ( $E_{\text{pit}} \sim -0.68 \pm 0.02 \text{ V}_{\text{SCE}}$ ). However, interactions between aggressive anions, such as chlorides ( $\text{Cl}^-$ ), with the passivating Al oxide may occur at potentials ( $E$ )  $< E_{\text{pit}}$ .(1) This research examines the interactions between  $\text{Cl}^-$  and the passive film on Al at  $E < E_{\text{pit}}$  in order to determine the role of  $\text{Cl}^-$  in the breakdown of passivity.

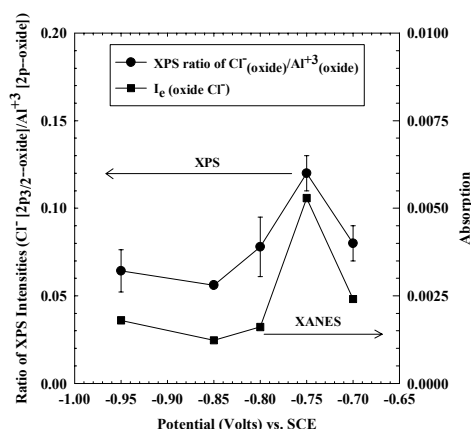
**Methods and Materials:** High purity polycrystalline Al (99.997% Al) was used for testing. Al samples were tested in deaerated 0.1 M NaCl solution at room temperature. A three-electrode electrochemical cell, with a saturated calomel reference electrode, was used. The samples were potentiostatically polarized at potentials below  $E_{\text{pit}}$  of Al, and were held at each potential for 3 hours. Surface analysis of the anodically polarized samples were conducted using X-ray photoelectron spectroscopy (XPS) with  $\text{Mg K}_{\alpha}$  X-rays, and X-ray absorption near edge spectra (XANES) to record changes and shifts in the K-edge structure of  $\text{Cl}^-$  (2833 eV). Both electron yield and X-ray fluorescence XANES were recorded.

**Results and Conclusions:** Two distinct peaks were observed in the electron yield spectra of  $\text{Cl}^-$ . The  $\text{Cl}^-$  XANES peak measured by electron yield at 2833 eV,  $I_e(\text{surface})$ , was attributed to  $\text{Cl}^-$  on the surface of the Al oxide, while the peak at 2836 eV,  $I_e(\text{oxide})$ , is associated with  $\text{Cl}^-$  within the Al oxide, or at the oxide/metal interface. An increase and then a decrease in  $I_e(\text{surface})$  during polarization from -0.950 to -0.800 V suggests an increasing and a diminishing surface coverage by  $\text{Cl}^-$ , as shown in Figure 1. Further polarization from -0.800 to -0.750 V produced increases in  $I_e(\text{surface})$ , which reflects a renewed surface coverage by  $\text{Cl}^-$ . Moreover,  $I_e(\text{oxide})$  also increased during anodic polarization from -0.850 to -0.750 V (Figure 2). The increase in  $I_e(\text{oxide})$  can be attributed to  $\text{Cl}^-$  incorporation into the oxide. However, anodic polarization from -0.750 to -0.700 V resulted in a decrease in  $I_e(\text{oxide})$ . Similar measurements of surface and bulk  $\text{Cl}^-$  were recorded by XPS (Figures 1 and 2). Such a decrease in measured  $I_e(\text{oxide})$  can be explained by, albeit not limited to: i) oxide thinning during polarization, where the oxide dissolution rate is greater than the rate of  $\text{Cl}^-$  uptake into the oxide, ii) oxide thickening that leads to increased attenuation of the secondary electron signal from  $\text{Cl}^-$  anions, which migrated from the solution/oxide interface to the oxide/metal interface, or iii) migration of  $\text{Cl}^-$  from the surface toward the oxide/metal interface resulting in a loss of signal due to attenuation. Al oxide thickness, as measured by XPS, remained relatively constant during anodic polarization from -0.950 to -0.800 V. However, the oxide thickness decreased from approximately 5 nm to 3.8 nm during polarization from -0.800 to -0.750 V.

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**Figure 1:**  $I_e$  (surface) and XPS for Al measured in Figure 1:  $I_e$  (surface) and XPS for Al measured in 0.1 M NaCl.



**Figure 2:**  $I_e(\text{oxide})$  and XPS for Al measured in 0.1 M NaCl.